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(54) HEAT INSULATING FOAM AND ITS PRODUCTION

(57)Abstract:
PURPOSE: To obtain a heat insulating foam free from swelling of a resin due to a foaming agent liquefied in cells and excellent in heat insulating property.
CONSTITUTION: This heat-insulating foam comprises a rigid urethane foam having closed cells and the pressure of a vaporized foaming agent contained in the closed cells is ≤100mmHg at 25° C. In forming a rigid urethane resin having closed cells by vaporizing and expanding the foaming agent by reaction heat of a polyol with a polyisocyanate in a closable container, the interior of the container is evacuated by a vacuum pump and foaming is carried out under a pressure of ≤300mmHg and the pressure in the container is controlled so that cell diameter is ≥ 10μm and ≤300μm and the foaming agent is packed into the closed cells so that the pressure in the closed cell is ≤100mmHg at 25° C.

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CLAIMS

[Claim(s)]
[Claim 1] Heat insulation foam characterized by the pressure of the gasificated foaming agent which consists of hard urethane resin foam which has a closed cell containing a foaming agent, and is contained in said closed cell being 100 or less mmHgs at 25 degrees C.
[Claim 2] Heat insulation foam according to claim 1 said whose foaming agent is a with a molecular weight of 70 or more compound in 150 degrees C or less of boiling points and whose pressure of the gasificated foaming agent which is contained in a closed cell is 1 or more mmHgs at 25 degrees C.
[Claim 3] Heat insulation foam according to claim 2 chosen from the group which said foaming agent becomes from the hydrocarbon which has the cyclic hydrocarbon and the 4th class carbon structure of having one or more rings.
[Claim 4] Heat insulation foam according to claim 1 said whose foaming agent is the compound of 170 degrees C or less of boiling points and whose pressure of the gasificated foaming agent which is contained in a closed cell is 1 or less mmHg at 25 degrees C.
[Claim 5] Heat insulation foam according to claim 1 which is the compatibility compound which said foaming agent dissolves in polyol.
[Claim 6] At least one sort of with a molecular weight of 70 or more liquids are mixed at a rate of 0.4 mols/kg or less to polyol by 150 degrees C or less of boiling points as a foaming agent. The mixture furthermore mixed with the poly isocyanate is made to react into [which can be sealed] a container. It faces forming the rigid urethane foam which said foaming agent is made to evaporate and foam with the heat of reaction of said polyol and said poly isocyanate, and has a closed cell. By controlling the pressure in said container so that the diameter of air bubbles is set to 10 micrometers or more 300 micrometers or less, while decompressing the pressure in said container using a vacuum pump and making it foam by the pressure of 300 or less mmHgs The manufacture approach of the heat insulation foam characterized by making it filled up with said foaming agent in said closed cell so that it may become the pressure of 100 or less mmHgs at 25 degrees C.
[Claim 7] The manufacture approach of the heat insulation foam according to claim 6 which said foaming agent is the compound of 95 degrees C or more of boiling points, and makes foaming temperature in said container the temperature of 60 degrees C or more.
[Claim 8] The manufacture approach of the heat insulation foam according to claim 7 chosen from the group which said foaming agent becomes from the cyclic ether which has the hydrocarbon which has two or more rings, and two or more oxygen.
[Claim 9] At least one sort of liquids of 170 degrees C or less of boiling points as a foaming agent are mixed at a rate of 0.004 mols/kg or less to polyol. The mixture furthermore mixed with the poly isocyanate is made to react into [which can be sealed] a container. It faces forming the rigid urethane foam which said foaming agent is made to evaporate and foam with the heat of reaction of said polyol and said poly isocyanate, and has a closed cell. Decompress the pressure in said container using a vacuum pump, and foaming is started by the pressure of 300 or less mmHgs. By controlling the pressure in said container so that the diameter of air bubbles is set to 10 micrometers or more 300 micrometers or less, while considering as the pressure of 0.1 or

less mmHgs at the time of foaming termination The manufacture approach of the heat insulation foam characterized by making it filled up with said foaming agent in said closed cell so that it may become the pressure of 1 or less mmHg at 25 degrees C.
[Claim 10] The manufacture approach of heat insulation foam according to claim 7 or 9 that a foaming agent is a reactant foaming agent, said reactant foaming agent is solidified by the cellular wall surface, and the inside of air bubbles is decompressed after reaction / foaming process of polyurethane.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the foaming heat-insulating element used for a refrigerator, a freezer, etc.
[0002]
[Description of the Prior Art] In recent years, environmental destruction by chlorofluocarbon, such as ozone layer depletion or warming of the earth, serves as a social concern, and reduction of the chlorofluorocarbon (trichloromonofluoromethane etc.) which is the foaming agents of heat insulation foam, such as rigid urethane foam, has been a big technical problem. For this reason, 1 which is matter with ozone modulus of rupture small as foaming agent, and 1-dichloro-1-fluoro ethane (HCFC-141b), 1, and 1-dichloro - 2, 2, and 2-trifluoro ethane (HCFC-123) etc. is used, and polyurethane foam is formed. Moreover, the manufacturing method of the polyurethane foam which uses hydrocarbons, such as a small cyclopentane of effect in environmental destruction, such as ozone layer depletion and global warming, as a foaming agent is also known well (for example, the collection of announcement drafts of the May, 1993 polyurethane international forum 93 197 pages, gel HARUTOHAIRIHHI Yoshitoku Kihara "pentane foaming rigid urethane foam").
[0003]
[Problem(s) to be Solved by the Invention] In conventional heat insulation foam, absorption of the foaming agent by resin having taken place, having connected this with the swelling of the resin section, and having not maintained detailed air bubbles and thin box-frame construction, but having un-arranged [to which a heat insulation property falls], since the inside of the closed cell of polyurethane foam was filled with the foaming agent near ordinary pressure. In order for the part which returns to ordinary temperature or becomes to liquefy and to carry out the adhesion dissolution at resin even if it evaporates with the heat of reaction at the time of polyurethane formation at the time of foaming if a foaming agent with the comparatively high boiling point is used especially, the fall of heat insulation property tends to take place. For example, the vapor pressure in a closed cell [in / in the cyclopentane (49 degrees C of boiling points) used as a hydrocarbon system foaming agent / 25 degrees C] is more than 300mmHg extent, and about the one half of the amount used for foaming has liquefied.
[0004] Moreover, the foaming agent with the pressure of the foaming agent which remains in heat insulation foam high [many] since many are inflammability of a hydrocarbon system will increase the ignition at the time of manufacture and use, and the danger of explosion. Furthermore, if hydrocarbons other than a cyclopentane are used as a foaming agent, what has molecular weight lower than this has thermal conductivity highly difficult [for the top where the boiling point is low] to use. Moreover, some which have high molecular weight had the problem that stopped evaporating with the heat of reaction of polyurethane easily, and the duty of a foaming agent was not achieved according to the boiling point being high, although thermal conductivity was low.
[0005] This invention aims at offering the heat insulation foam which there is no swelling of the resin by the foaming agent liquefied within air bubbles in view of the above, and consists of

adiathermic outstanding hard foaming urethane resin. This invention is also set again, when using an inflammable foaming agent, and it aims at offering the heat insulation foam by which the ignition at the time of manufacture and use and the danger of explosion were reduced. This invention aims at offering the approach of it being efficient and manufacturing the heat insulation foam which consists of hard foaming urethane resin which has the adiathermic outstanding closed cell.

[0006]

[Means for Solving the Problem] The heat insulation foam of this invention consists of hard urethane resin foam which has a closed cell containing a foaming agent, and the pressure of the gasificated foaming agent which is contained in said closed cell is characterized by being 100 or less mmHgs at 25 degrees C.

[0007] Here, said foaming agent is a with a molecular weight of 70 or more compound in 150 degrees C or less of boiling points, and it is desirable for the pressure of the gasificated foaming agent which is contained in a closed cell to be 1 or more mmHgs at 25 degrees C.

[0008] Moreover, as for said foaming agent, it is desirable that it is the compound chosen from the group which consists of a hydrocarbon which has the cyclic hydrocarbon and the 4th class carbon structure of having one or more rings.

[0009] In other modes of the above-mentioned heat insulation foam, said foaming agent is the compound of 170 degrees C or less of boiling points, and the pressure of the gasificated foaming agent which is contained in said closed cell is 1 or less mmHg at 25 degrees C.

[0010] Furthermore, as for said foaming agent, it is desirable that it is the compatibility compound which dissolves in polyol. Such a compatibility compound has the desirable compound chosen from the group which consists of ester, the ether, a tertiary amine, and a ketone.

[0011] The manufacture approach of the heat insulation foam of this invention mixes at least one sort of with a molecular weight of 70 or more liquids at a rate of 0.4 mols/kg or less to polyol by 150 degrees C or less of boiling points as a foaming agent. The mixture furthermore mixed with the poly isocyanate is made to react into the container which can be sealed. It faces forming the rigid urethane foam which said foaming agent is made to evaporate and foam with the heat of reaction of said polyol and said poly isocyanate, and has a closed cell. By controlling the pressure in said container so that the diameter of air bubbles is set to 10 micrometers or more 300 micrometers or less, while decompressing the pressure in said container using a vacuum pump and making it foam by the pressure of 300 or less mmHgs It is characterized by making it filled up with said foaming agent in said closed cell, so that it may become the pressure of 100 or less mmHgs at 25 degrees C.

[0012] In here, said foaming agent is the compound of 95 degrees C or more of boiling points, and it is desirable to make foaming temperature in said container into the temperature of 60 degrees C or more.

[0013] Moreover, as for said foaming agent, it is desirable to use the compound chosen from the group which consists of cyclic ether which has the hydrocarbon which has two or more rings, and two or more oxygen.

[0014] Furthermore, the manufacture approach of the heat insulation foam of this invention mixes at least one sort of liquids of 170 degrees C or less of boiling points as a foaming agent at a rate of 0.004 mols/kg or less to polyol. The mixture furthermore mixed with the poly isocyanate is made to react into [which can be sealed] a container. It faces forming the rigid urethane foam which said foaming agent is made to evaporate and foam with the heat of reaction of said polyol and said poly isocyanate, and has a closed cell. Decompress the pressure in said container using a vacuum pump, and foaming is started by the pressure of 300 or less mmHgs. While considering as the pressure of 0.1 or less mmHgs at the time of foaming termination, the pressure in said container is controlled so that the diameter of air bubbles is set to 10 micrometers or more 300 micrometers or less, and you make it filled up so that it may become the pressure of 1 or less mmHg at 25 degrees C about said foaming agent in said closed cell.

[0015] Moreover, in the manufacture approach of the heat insulation foam of this invention, a foaming agent is a reactant foaming agent and it is desirable after reaction / foaming process of polyurethane that said reactant foaming agent is solidified by the cellular wall surface, and the

inside of air bubbles is decompressed.
[0016]
[Function] The heat insulation foam of this invention has the configuration by which the foaming agent gasificated in the closed cell as mentioned above was filled up with 25 degrees C by the pressure of 100 or less mmHgs. Since there are few amounts of the foaming agent which exists as a gas in air bubbles, swelling of the resin part accompanying the dissolution to the resin of a foaming agent cannot happen easily, and detailed air bubbles and thin box-frame construction are maintained. Consequently, the outstanding heat insulation property is realized. Moreover, since there are few amounts of foaming agents which remain in heat insulation foam, even if a foaming agent is inflammability, the flammability of heat insulation foam falls and the safety to the combustion at the time of use improves.
[0017] Moreover, it sets like 1 voice, a foaming agent is a with a molecular weight of 70 or more compound in 150 degrees C or less of boiling points, and the especially desirable pressure of the heat insulation foam of this invention with which said gasificated foaming agent is filled up in a closed cell is 1 or more mmHgs. According to this configuration, the molecular weight of a foaming agent can make it foam enough using the gas more than cyclopentane (molecular weight 70.14) extent. Consequently, thermal conductivity is low and serves as heat insulation foam which has the outstanding heat insulation property. The configuration of such a foaming heat-insulating element is realized by the first manufacture approach of this invention.
[0018] Furthermore, in other especially desirable modes of the heat insulation foam of this invention, a foaming agent is the compound of 170 degrees C or less of boiling points, and the pressure with which the foaming agent gasificated in the closed cell is filled up is 1 or less mmHg. According to this configuration, since the degree of vacuum in a closed cell is high, the heat insulation property which was very excellent is realized. Such a foaming heat-insulating element is realized by the second manufacture approach of this invention.
[0019] Moreover, when it is the compatibility compound which a foaming agent dissolves in polyol, it is desirable in order to give uniform and detailed cellular structure on the occasion of foaming under reduced pressure.
[0020] In the first manufacture approach of this invention, since a with a molecular weight of 70 or more liquid is used as a foaming agent at 150 degrees C or less of boiling points and it foams under reduced pressure of 300 or less mmHgs, under ordinary pressure, foaming which was excellent also in the foaming agent which does not evaporate and foam easily [since the boiling point is high], using this as a foaming agent since the boiling point fell with reduced pressure becomes possible. When using a foaming agent with the higher boiling point at this time, foaming becomes possible by making the pressure in the container at the time of foaming still lower than 300mmHg(s).
[0021] Moreover, under reduced pressure, since it is larger than the case where the volume when evaporating is ordinary pressure, foaming using a little foaming agent also becomes possible. Furthermore, only with the heat of reaction of resinification, since the specific heat, heat of vaporization, etc. are usually large, in order that a foaming agent with difficult foaming may also use only small quantity, it has the big description of a required heating value decreasing and it being said possible that foaming becomes. Moreover, as a foaming agent, the thing of 150 degrees C or less of boiling points when the vapor pressure in 25 degrees C is set to 1 or more mmHgs is used so that the pressure of a restoration gas may be set to 1 or more mmHgs. Good foaming is attained by carrying out like this. Moreover, since the amount of the foaming agent to be used is 0.4 mols/kg or less to polyol, even when a foaming agent with high vapor pressure with molecular weight comparatively low at about 70 is used, the pressure of the foaming agent in a closed cell is set to 100 or less mmHgs.
[0022] This first manufacture approach adjusts the diameter of air bubbles by controlling whenever [in the container which performs foaming further / reduced pressure] using a vacuum pump. By controlling whenever [reduced pressure], it becomes possible to decide the timing of a polyurethane formation reaction and foaming suitably, and has the very important description that the suitable diameter of air bubbles is realized. As for this, in the case of foaming under ordinary pressure, formation of polyurethane and the timing of foaming are contrastive with

having been decided in the boiling point of a foaming agent. That is, since foaming becomes slow and resin becomes hard even if air bubbles become large, heat required for foaming at a polyurethane formation reaction will not be obtained if the boiling point is too high or it is obtained, since resin is too soft, if the boiling point of a foaming agent is low and foaming is too early under ordinary pressure, sufficient increment in the volume does not take place. Therefore, only the foaming agent which has the boiling point from room temperature extent to about 50 degrees C was used. When the diameter of air bubbles is small, it is made early, as compared with the diameter of air bubbles of the foaming agent which the timing of suitable foaming changes the stage and rate of the reduced pressure initiation by the vacuum pump, and is obtained, when large, it is made later, and it is determined experimentally. At this time, although the diameter of air bubbles is adjusted to small 300-micrometer or less value of 10 micrometers or more in order to acquire a good heat insulation property, its about 60 micrometers are desirable from the ease of control.

[0023] Moreover, it is desirable to foam at the high temperature of 60 degrees C or more in this first manufacture approach using the foaming agent of 95 degrees C or more of boiling points as mentioned above. Since it is not necessary to make the pressure in a container extremely low, adjustment of the container internal pressure at the time of foaming becomes easy, and the diameter of air bubbles is made as for it to homogeneity. Moreover, since the boiling point can use effectively the very small gas of thermal conductivity with large molecular weight above 95 degrees C, the heat insulation foam superior to that of a heat insulation property is obtained.

[0024] In the second manufacture approach of this invention, in order to make it foam under reduced pressure, the increment in the volume is large, and foaming sufficient with the foaming agent of the ultralow volume of 0.004 mols/kg is attained to polyol. Moreover, this second manufacture approach adjusts the diameter of air bubbles by controlling whenever [in the container which performs foaming / reduced pressure] like the first manufacture approach using a vacuum pump. Therefore, it has the very important description that decide the timing of a polyurethane formation reaction and foaming suitably by controlling whenever [reduced pressure] similarly, and control of the diameter of air bubbles is attained. However, since there are very few amounts of the foaming agent to be used, after foaming initiation must fully lower a pressure by the time of foaming termination, and the pressure at the time of foaming termination is set to 0.1 or less mmHgs.

[0025]

[Example] Next, this invention is explained based on a desirable example. In this invention, especially the thing for which the thermal conductivity of a foaming agent is reduced, it is 150 degrees C or less of boiling points and 70 or more molecular weight as a foaming agent, and a compound with larger molecular weight than cyclopentane extent is used in order to raise the heat insulation property of the foam obtained, and the pressure of the gasificated foaming agent in a closed cell is set to 1 or more mmHgs is desirable. When this has the too low pressure of a with a molecular weight [in a closed cell] of 70 or more gas, it is because it becomes impossible to disregard existence of the residual gas as an impurity with high thermal conductivity with small molecular weight within a closed cell.

[0026] The hydrocarbon which has the cyclic hydrocarbon or the 4th class carbon structure of having one or more rings from a viewpoint of thermal conductivity, as a with a molecular weight of 70 or more compound at 150 degrees C or less of boiling points is desirable for improvement in a heat insulation property. As this example, there are the cyclopentane (molecular weight 70.14, 49 degrees C of boiling points) of a cyclic hydrocarbon, a cyclohexane (molecular weight 84.16, 80.7 degrees C of boiling points), a cyclohexene (molecular weight 82.15, 83 degrees C of boiling points), 1, 4-cyclohexadiene (molecular weight 80.13, 81 degrees C of boiling points), 1, 3-cyclohexadiene (molecular weight 80.13, 80 degrees C of boiling points), bicyclo heptadiene (molecular weight 92.14, 89 degrees C of boiling points), NORUBONIREN (molecular weight 94.16, 96 degrees C of boiling points), Moreover, as a hydrocarbon which has the 4th class carbon structure, there is a 2 and 2-dimethyl butane (molecular-weight 86.18, 50 degrees C of boiling points), 2, and 3-dimethyl-2-butene (molecular weight 84.16, 73 degrees C of boiling points) etc.

[0027] Furthermore, especially since [that molecular weight is large] the fluorinated compound

has low thermal conductivity, it is desirable. As this example, there are a perfluoro decalin (molecular weight 462.1, 141 degrees C of boiling points), a perfluoro methylcyclohexane (molecular weight 350.7, 78 degrees C of boiling points), perfluoro methylcyclopentane (molecular weight 300.05, 57 degrees C of boiling points), etc.

[0028] Moreover, in the heat insulation foam of this invention, the gasificated foaming agent is smaller than molecular weight 70, and especially the configuration whose pressure with which this gasificated foaming agent is filled up in a closed cell is 1 or less mmHg is desirable. Usually, although the foaming agent with molecular weight smaller than 70 is unsuitable as a foaming agent for heat insulation foam since molecular weight is small, and thermal conductivity is high, it is making filling pressure in a closed cell extremely low, and serves as heat insulation foam which has the outstanding heat insulation property.

[0029] Moreover, in order to form a closed cell uniform and detailed as a foaming agent of the heat insulation foam of this invention described so far, the compound which has polyol and compatibility is desirable. As this compatibility compound, there are ester, the ether, a tertiary amine, and a ketone. For example, there are methyl propionate (molecular weight 88.11, 79 degrees C of boiling points), methyl iso butyrate (molecular weight 102.13, 90 degrees C of boiling points), a tetrahydrofuran (molecular weight 72.11, 66 degrees C of boiling points), 1, 3-dioxolane (molecular weight 74.08, 74 degrees C of boiling points), triethylamine (molecular weight 101.19, 89 degrees C of boiling points), 3-methyl-2-butanone (molecular weight 86.13, 93 degrees C of boiling points), etc.

[0030] There are two kinds of following manufacture approaches as an approach of realizing the configuration of especially desirable heat insulation foam described above. The first manufacture approach mixes further with the poly isocyanate what mixed the with a molecular weight of 70 or more liquid at a rate of 0.4 mols/kg or less to polyol by 150 degrees C or less of boiling points as a foaming agent, and carries out evaporation foaming of this within the container which was decompressed using the vacuum pump and which can be sealed. In order to foam under reduced pressure, it foams to the efficient big volume and becomes that what is necessary is just to use a foaming agent 0.4 mols [/kg] or less to polyol as a result. Moreover, at the time of this evaporation foaming, the pressure in a container is too high, and foaming is overdue, or the diameter of air bubbles is controlled by adjusting to a moderate pressure so that it is too low and growing gigantic of bumping or air bubbles does not take place. To polyol, since it is few in kg and 0.4 mols /or less, the maximum vapor tension in air bubbles also falls, and the amount of the foaming agent to be used becomes the pressure of 100 or less mmHgs. Since what has large molecular weight has the boiling point and large heat of vaporization, it does not fully foam only with the heat obtained at the reaction of the poly isocyanate and polyol in many cases, but in order to end with the heat which provides the temperature up of a little foaming agent, and evaporation according to this approach, foaming takes place easily.

[0031] Moreover, if the pressure in air bubbles becomes small too much as already stated, the effect of a gas with small thermal conductivity, such as air which is an impurity, may come out, and a heat insulation property may worsen. Therefore, the pressure in air bubbles needs to have 1 or more desirable mmHgs, the boiling point of a foaming agent needs to be 150 degrees C or less in this case, and the amount used needs to be 0.004 mols/kg or more to polyol. In the same reason, as for the pressure in air bubbles, it needs to be still more desirable that they are 10 or more mmHgs, the boiling point of a foaming agent needs to be 115 degrees C or less in this case, and the amount of foaming agents needs to be 0.04 mols/kg or more. Moreover, since it becomes easy for the one to some extent where the boiling point is higher to control foaming, without being influenced by the temperature decided with heat of reaction in order to make it foam under reduced pressure like this invention and to control a foaming stage, 75 degrees C or more of boiling points are desirable.

[0032] Moreover, about the first manufacture approach of this heat insulation foam, it is desirable to make it foam at the temperature of 60 degrees C or more using at least one kind of liquid of 95 degrees C or more of boiling points as a foaming agent. The molecular weight of the liquid of 95 degrees C or more of boiling points is also large, since the thermal conductivity of a gaseous state is also small, it is desirable as a foaming agent, but since maximum vapor tension

is low, it needs to keep still lower the pressure in the container at the time of foaming compared with the low thing of the boiling point. However, if the heat insulation foam raw material containing a foaming agent is poured in, with change of that vapor pressure and volume in a container, the pressure in a container will be changed, and the rate of this pressure fluctuation is so large that an early pressure is low, and this will produce the heterogeneity of the air bubbles in heat insulation foam, and will tend to lead to the fall of a heat insulation property. Therefore, an initial pressure is maintained at a to some extent high pressure, and manufacture of heat insulation foam becomes [the direction which raises the temperature at the time of foaming] easy. It is 60 degrees C or more in temperature, and is the container internal pressure 100 - more than 200mmHg extent, and by making it foam, the diameter of air bubbles is uniform and, specifically, heat insulation foam excellent in heat insulation property is obtained easily. Moreover, if the high thing of OH ** is used as polyol, temperature of the reaction time of the poly isocyanate and polyol can be made high, and, thereby, can set up foaming temperature highly.

[0033] It is possible to use suitably the cyclic ether which has the hydrocarbon which has two or more rings, or two or more oxygen as a liquid of 95 degrees C or more of boiling points. such a hydrocarbon and cyclic ether -- carrying out -- there is KUADORISAI clan (molecular-weight 92.14, 108 degrees C of boiling points), 1,4-dioxane (molecular-weight 88.1, 101 degrees C of boiling points), 1, and 4-JIOKISEN (molecular weight 86.1, 95 degrees C of boiling points) etc.

[0034] Moreover, it is desirable for the pressure with which the foaming agent gasificated in the closed cell is filled up as heat insulation foam of this invention especially to be 1 or less mmHg. The heat insulation property which was excellent since the degree of vacuum in a closed cell was very high as already stated is realized. The configuration of such a foaming heat-insulating element is realized by the second manufacture approach of this invention. In this approach, although it is made to foam under reduced pressure as well as the first manufacture approach, there is the description which makes the foaming agent of the ultralow volume of 0.004 mols/kg foam to a product generally by the quite low pressure to polyol. Thus, since the foaming agent to be used is a minute amount, the pressure of the foaming agent which remains in a closed cell becomes very low with 1 or less mmHg. Moreover, there is the very important description that control becomes possible about the diameter of air bubbles by adjusting a pressure and taking the timing of an urethane formation reaction and foaming also by this second manufacture approach. Moreover, since there are few amounts of a foaming agent, there can be little energy which evaporation takes, and can end and the boiling point can also use the high, large compound of heat of vaporization. Moreover, since foaming will become difficult if too few, as for the amount of a foaming agent, it is desirable to use 0.001 mols /or more kg.

[0035] In addition to the foaming agent used by the first manufacture approach, the foaming agent which has the boiling point in a 150 to 170 degrees C pyrosphere can be used for the foaming agent used for the second manufacture approach of this this invention. This is because the vapor pressure in a closed cell becomes low and there should just be vapor pressure in 25 degrees C more than 0.2mmHg extent. Moreover, a foaming agent with high thermal conductivity with small molecular weight can also be used. This has a pressure as low as 1 or less mmHg in air bubbles, and is because it becomes regardless of the heat insulation property of heat insulation foam at the thermal conductivity of the gas in a closed cell. As a concrete foaming agent, there are a dicyclopentadiene (molecular weight 132.21, 170 degrees C of boiling points), a perfluoro-1-methyl decalin (molecular weight 512.11, 159 degrees C of boiling points) to have the boiling point in a pyrosphere, etc. Moreover, about what has low molecular weight, since control of foaming under reduced pressure will become difficult if the boiling point is too low, it is desirable to have the boiling point about 50 degrees C or more. Moreover, since there are very few amounts of the foaming agent used by this second manufacture approach, mixing with polyol more at homogeneity is important for a foaming agent, and its compatibility compounds, such as the ether excellent in compatibility with the already described polyol, a ketone, and tertiary amine, are desirable especially as a foaming agent.

[0036] Moreover, in order to prevent the heat insulation property of a foaming heat-insulating element worsening when gases, such as air with high thermal conductivity other than a foaming

agent, blend, it is desirable to permute the inside of the container made reduced pressure with the foaming agent gasificated beforehand. Moreover, a foaming agent may consist of a reactant foaming agent in the heat insulation foam of this invention. A reactant foaming agent is a foaming agent solidified by a certain chemical reaction after foaming, it mixes with an urethane raw material and this is used. In this way, the heat insulation foam which the inside of air bubbles was decompressed and excelled [solidify / this reactant foaming agent / by the cellular front face] in the heat insulation property is obtained after the foaming process of polyurethane. As such a reactant foaming agent, the compound which has either [at least] an amino group or a hydroxyl group is desirable, and these compounds delay a stage from foaming and are solidified by reacting with the poly isocyanate. It is also possible to make it foam using the liquid of polymerization nature as a foaming agent, to delay a stage otherwise, and to carry out polymerization immobilization of the foaming agent according to an operation of a polymerization catalyst.

[0037] As an approach of making a stage delaying and solidifying from foaming, the compound which has an amino group or a hydroxyl group is used as a core, and after destroying a microcapsule with the heat of reaction of the poly isocyanate and polyol as a wallplate and a microcapsule and making thermoplastics foam, the approach of solidifying by the reaction with the poly isocyanate is. It is effective for others to use tertiary alcohol with a comparatively slow reaction with the poly isocyanate etc. After making tertiary alcohol etc. foam with the heat of reaction of the poly isocyanate and polyol, it is possible to make said alcohol and isocyanate react and to solidify. Moreover, a phenol, a thiol, a carboxylic acid, an acid amide, etc. are one of those have slow a reaction although it reacts with isocyanate and possible using as a reactant foaming agent. As alcohol suitably used especially as a reactant foaming agent, there are a tertiary butanol (molecular weight 74.12, 83 degrees C of boiling points), hexafluoro-2-methyl isopropanol (molecular weight 182.0, 60 degrees C of boiling points), and a perfluoro tertiary butanol (molecular weight 236.05, 44 degrees C of boiling points).

[0038] Moreover, in the case of the heat insulation foam for refrigerators, the container used with the configuration of this invention described in the top usually consists of a metallic cabinet and an inner case made of resin. Although the pressure of several 100 mmHg(s) joins this container at the time of reduced pressure, it is possible to prevent the big deformation by said pressure impression by choosing the structure containing the ingredient and thickness of a tank and an inner case. Or not only the inside of a container but the outside of a container and the approach except the pressure which joins a container as reduced pressure can also be used. Moreover, after resin spreads in a large area for evasion of bumping, or uniform cellular formation, it can also be made to foam at the time of impregnation of the resin raw material containing polyol and the poly isocyanate. Furthermore, after pouring in a resin ingredient, it becomes possible by carrying out reduced pressure control of the inside of a container gradually.

[0039] In order that the polyol used for this invention may obtain a degree of hardness besides the polyether system polyol currently used conventionally and polyester system polyol, or in order to control reactivity, the polyol which has in intramolecular many hydroxyl groups compounded from polyhydric alcohol is suitable. Moreover, since there are few amounts of the foaming agent to be used, polyol with low viscosity is desirable. The poly isocyanate to which a diphenylmethane diisocyanate system, a tolylene diisocyanate system, a xylylene diisocyanate system, a meta-xylylene diisocyanate system, a hexamethylene di-isocyanate system, the lysine diisocyanate system, the isophorone diisocyanate system, the trimethyl-hexamethylene-di-isocyanate system, the dimer acid diisocyanate system, etc. are suitable, and the isocyanate used for this invention gave these fire retardancy is most suitable.

[0040] The catalyst used in this invention is good to choose the most effective catalyst with the reactivity of an urethane raw material, such as a gelation catalyst, a bubble-ized catalyst, and a delay catalyst. Although the catalysts generally used are the third class amine and an organometallic compound, there are amines monoamines, diamines, triamine, annular amines, and alcoholic, ether amines, etc. in an amine system catalyst. In an organometallic compound, an organic tin compound is used best. The catalyst for a general formula is used in this invention.

However, it is required to mix the catalyst of various kinds [**** / using properly depending on the boiling point]. Moreover, the foam stabilizer used for this invention has a common alkyl SHIRAN polyoxyalkylene copolymer. A silicon system foam stabilizer shows the outstanding addition effectiveness, although the effectiveness differs. In addition, the compatibility of a raw material is raised and it becomes a cellular nucleus, and if surface tension is reduced and the air bubbles under foaming are stabilized, it can use.

[0041] the following concrete examples — setting — as Catalyst A — the Kao Corp. make — as KAORAIZA No.1 and a foam stabilizer A — the poly isocyanate of amine equivalent 170 was used as hydroxyl value 600 mgKOH/g and poly isocyanate A by aromatic amine system polyether polyol as hydroxyl value 500 mgKOH/g and polyol B by aromatic amine system polyether polyol as the product F373 made from Shin-etsu Chemistry, and polyol A.

[0042] In [example 1] this example, the heat insulation foam to which it comes to fill up this foaming agent by the pressure of 100 or less mmHgs in a closed cell at 150 degrees C or less of boiling points using a with a molecular weight of 70 or more foaming agent was formed under reduced pressure. The weight ratio of the used raw material is as follows. Polyol A / foam stabilizer A / catalyst A / foaming agent A / poly isocyanate =100/3/2/2.8/165. 2 and 2-dimethyl butane (molecular weight 86.2, 50 degrees C of boiling points) which is the hydrocarbon which has the 4th class carbon structure as a foaming agent A was used. The concentration to the polyol of a foaming agent is 0.4 mols/kg. First, Polyol A, Catalyst A, and the foam stabilizer A were mixed, and the poly isocyanate A was mixed further. This resin raw material was poured in from that inlet into the container which consists of a metallic cabinet and an inner case made of resin and which can be sealed, and foaming of the hard urethane heat insulation foam was carried out. At this time, the inside of a container was beforehand changed into the reduced pressure condition of 400mmHg(s) through the exhaust port with the vacuum pump. After impregnation, the inlet exhausted according to advance of a polyurethane formation reaction, and performed foaming by the pressure of 300 or less mmHgs so that it might close and fluctuation of the pressure in a container might become small by the valve installed in the exhaust port. In addition, the pressures in the container at the time of foaming initiation were 300mmHg(s), and temperature was 30 degrees C. After foaming finished, it was left on the 1st, making the inside of a container reduced pressure. In this way, the pressures in the air bubbles which ground the obtained heat insulation foam and were computed from the amount of foaming agents which came out, and the volume of the air bubbles for which it asked from the consistency of foam and resin were 90mmHg(s). Moreover, the diameter of average air bubbles of a closed cell was 220 micrometers.

[0043] By the formula of polyol / foam stabilizer A / catalyst A / foaming agent A / poly isocyanate =100/3/2/22/165, the weight ratio of the [example 1 of comparison] raw material performs foaming to the bottom of ordinary pressure. The concentration to the polyol of a foaming agent is 0.4 mols/kg. In this way, when cellular internal pressure was computed like the example 1 about the obtained foam, it had liquefied about the one half of the foaming agent used by 320mmHg.

[0044] Heat insulation property was compared as follows before grinding about the foam obtained in the example 1 and the example 1 of a comparison. That is, in the 25-degree C interior of a room, heat insulation foam with a thickness of 5cm was carried on the 50-degree C hot plate, and the temperature gradient of the top face and inferior surface of tongue was measured. From the comparison of the thermal conductivity for which it asked from this temperature gradient, the heat insulation foam of an example 1 was excellent in the heat insulation property 8% compared with the heat insulation foam of the example 1 of a comparison. Moreover, when the fire-resistant sex test was performed, the heat insulation foam of an example 1 showed fire retardancy better than the heat insulation foam by which foaming was carried out under the ordinary pressure of the example 1 of a comparison. Since suitable cellular structure was formed by that there are few amounts of the foaming agent contained in the closed cell of foam, and there are also few amounts of the foaming agent to liquefy since the heat insulation foam of an example 1 is foaming using a little foaming agent under reduced pressure, and having performed timing of a polyurethane formation reaction and foaming by

accommodation of whenever [reduced pressure], this is considered.
[0045] In [example 2] this example, the compound which has polyol and compatibility as a foaming agent is used. The weight ratio of the used raw material is as follows. Polyol A / foam stabilizer A / catalyst A / foaming agent B / poly isocyanate =100/3/2/2.8/165. As a foaming agent B, the ether system compound tetrahydrofuran with polyol and compatibility was used. The concentration to the polyol of a foaming agent is 0.39 mols/kg. Heat insulation foam was obtained almost like the example 1. However, foaming was performed under the pressure of 200 or less mmHgs. The pressures at the time of foaming initiation were 200mmHg(s), and temperature was 50 degrees C. When the pressure in the air bubbles of the obtained foam was computed like the example 1, it was 80mmHg(s). Moreover, the diameter of average air bubbles of a closed cell was 110 micrometers. About the obtained heat insulation foam, fire retardancy and a heat insulation property were measured like the example 1. About fire retardancy, good fire retardancy was shown compared with the example 1 of a comparison like the example 1. Moreover, about the heat insulation property, it improved 20% as compared with the example 1. Compatibility with polyol becomes good by using an ether system compound as a foaming agent, and since uniform and detailed air bubbles were formed, the improvement in this heat insulation property is considered.
[0046] In [example 3] this example, the reactant foaming agent which has a hydroxyl group as a foaming agent is used. The weight ratio of the used raw material is as follows. Polyol A / foam stabilizer A / catalyst A / foaming agent C / poly isocyanate =100/3/2/2.7/180. The tertiarybutyl alcohol which has a hydroxyl group was used as a foaming agent C. The concentration to the polyol of a foaming agent is 0.36 mols/kg. Moreover, it permuted so that 200mmHg hidden total pressure might be beforehand set to 240mmHg(s) in the steam of the foaming agent tertiarybutyl alcohol which uses the inside of a container. Moreover, the pressure at the time of foaming initiation was made to 150mmHg(s), temperature was made into 45 degrees C, and it was made to foam by the pressure of 150 or less mmHgs. Others formed heat insulation foam like the example 1. When the pressure in the air bubbles of the obtained foaming heat-insulating element was computed like the example 1, it was 1 or less mmHg. Moreover, the diameter of average air bubbles of a closed cell was 80 micrometers.
[0047] Heat insulation foam was formed using the tertiarybutyl alcohol as a foaming agent C under the [example 2 of comparison] ordinary pressure. In addition, the container preceded paying a polyurethane raw material and was heated at 50 degrees C. The weight ratio of the used raw material is as follows. Polyol A / foam stabilizer A / catalyst A / foaming agent C / poly isocyanate =100/3/2/30/180.
[0048] Fire retardancy and a heat insulation property were measured about the heat insulation foam obtained in the example 3 and the example 2 of a comparison. The heat insulation foam of an example 3 showed good fire retardancy compared with the example 2 of a comparison. Moreover, about the heat insulation property, it improved 32% compared with the example 2 of a comparison. Moreover, the example 2 of a comparison of the time amount needed after foaming by the time it reached the aforementioned heat insulation property, i.e., the time amount which a reactant foaming agent requires for solidifying enough, was as longer as 5 times of the foaming heat-insulating element of an example 3. The solid state of the tertiarybutyl alcohol which is the reactant foaming agent which has the hydroxyl group used as a foaming agent progresses more efficiently, and since the pressure in air bubbles reached the high degree of vacuum by having fallen further, the improvement in this heat insulation property is considered. Since it foamed under reduced pressure, this has the little amount of the foaming agent which should be solidified, ends, and is considered because the solid state progressed efficiently as a result.
[0049] In [example 4] this example, using the compound of 95 degrees C or more of boiling points as a foaming agent, temperature at the time of foaming was made into 60 degrees C or more, and heat insulation foam was formed. The weight ratio of the used raw material is as follows. Polyol B / foam stabilizer A / catalyst A / foaming agent D / poly isocyanate =100/3/2/3.4/165. As a foaming agent D, the boiling point used the hydrocarbon KUADORISAI clan (molecular weight 92.14, 108 degrees C of boiling points) 95 degrees C or more. The concentration to the polyol of a foaming agent is 0.37 mols/kg. The pressure in 69 degrees C

and a well-closed container was set to 100mmHg(s) for the temperature at the time of foaming initiation, and also heat insulation foam was obtained like the example 1. When the pressure in the air bubbles of the obtained foaming heat-insulating element was computed like the example 1, it was 33mmHg(s). Moreover, the diameter of average air bubbles of a closed cell was 35 micrometers.

[0050] Foaming was tried by the formula of the following [the bottom of the [example 3 of comparison] ordinary pressure]. Polyol B / foam stabilizer A / catalyst A / foaming agent D / poly isocyanate =100/3/2/30/180. However, foaming did not fully take place but the volume of heat insulation foam became small.

[0051] Fire retardancy and a heat insulation property were measured about the heat insulation foam obtained in the example 4 and the example 3 of a comparison. About fire retardancy, the direction of an example 4 showed good fire retardancy compared with the example 3 of a comparison. Moreover, the heat insulation property of an example 4 improved 90% 20% compared with the example 3 of a comparison as compared with the example 1. It is made 60 degrees C or more by the thermal conductivity of the gas in a closed cell having fallen upwards, since the compound which has the boiling point 95 degrees C or more as a foaming agent was used, and it is whenever [comparatively high reduced pressure], and since high quality heat insulation foam was obtained, it is considered [since foaming advanced, control of container internal pressure becomes easy, the improvement in this heat insulation property is uniform and].

[0052] In [example 5] this example, the high heat insulation foam of the degree of vacuum in a closed cell was formed using the foaming agent of ultralow volume. The weight ratio of the used raw material is as follows. Polyol A / foam stabilizer A / catalyst A / foaming agent E / poly isocyanate =100/3/2/0.02/180. The acetone (molecular weight 58.0) was used as a foaming agent E. The concentration to the polyol of a foaming agent is 0.0034 mols/kg. Before pouring the above-mentioned resin raw material into a container, the inside of a container was decompressed through the exhaust port with the vacuum pump, the acetone was poured in so that the acetone steam of 270mmHg might exist, total pressure in an early container was set to 330mmHg(s), and also foaming was performed like the example 1. In addition, the pressures at the time of foaming initiation were 220mmHg(s), and temperature was 40 degrees C. Moreover, the pressure in the exhaust port at the time of the completion of foaming was 0.1 or less mmHgs.

[0053] In this way, when the pressure in the air bubbles of the obtained heat insulation foam was computed like the example 1, it was 1 or less mmHg. Moreover, the diameter of average air bubbles of a closed cell was 70 micrometers. Moreover, fire retardancy and a heat insulation property were measured about the obtained heat insulation foam. The heat insulation foam of an example 5 showed good fire retardancy like the example 3, and showed [fire retardancy] the good property about the heat insulation property as well as an example 3. Since the amount of a foaming agent is a minute amount and ended by foaming under reduced pressure, this good fire retardancy and a heat insulation property are considered because the degree of vacuum in the closed cell of the obtained heat insulation foam became high.

[0054]

[Effect of the Invention] As mentioned above, according to this invention, the vapor pressure of the foaming agent in the air bubbles of heat insulation foam falls, and the heat insulation foam whose heat insulation property improved is obtained. Moreover, the foaming agents which liquefy and are absorbed by resin decrease in number, and the swelling of resin is avoided. Furthermore, since there are both few amounts used for manufacture and amounts which remain into a closed cell when using an inflammable foaming agent, the ignition at the time of manufacture and use and the danger of explosion become small, and safety improves.

[0055] Moreover, since it foams to this invention under reduced pressure, while being able to make it foam enough with a little foaming agent, a compound with small thermal conductivity with large molecular weight can be used as a foaming agent, and the heat insulation foam which has adiathermic [outstanding] can be efficiently obtained from the ability of the degree of vacuum in a closed cell to be further made high for a short time.

[Translation done.]

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TECHNICAL FIELD

[Industrial Application] This invention relates to the foaming heat-insulating element used for a refrigerator, a freezer, etc.

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PRIOR ART

[Description of the Prior Art] In recent years, environmental destruction by chlorofluocarbon, such as ozone layer depletion or warming of the earth, serves as a social concern, and reduction of the chlorofluorocarbon (trichloromonofluoromethane etc.) which is the foaming agents of heat insulation foam, such as rigid urethane foam, has been a big technical problem. For this reason, 1 which is matter with ozone modulus of rupture small as foaming agent, and 1-dichloro-1-fluoro ethane (HCFC-141b), 1, and 1-dichloro - 2, 2, and 2-trifluoro ethane (HCFC-123) etc. is used, and polyurethane foam is formed. Moreover, the manufacturing method of the polyurethane foam which uses hydrocarbons, such as a small cyclopentane of effect in environmental destruction, such as ozone layer depletion and global warming, as a foaming agent is also known well (for example, the collection of announcement drafts of the May, 1993 polyurethane international forum 93 197 pages, gel HARUTOHAIRIHHI Yoshitoku Kihara "pentane foaming rigid urethane foam").

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EFFECT OF THE INVENTION

[Effect of the Invention] As mentioned above, according to this invention, the vapor pressure of the foaming agent in the air bubbles of heat insulation foam falls, and the heat insulation foam whose heat insulation property improved is obtained. Moreover, the foaming agents which liquefy and are absorbed by resin decrease in number, and the swelling of resin is avoided. Furthermore, since there are both few amounts used for manufacture and amounts which remain into a closed cell when using an inflammable foaming agent, the ignition at the time of manufacture and use and the danger of explosion become small, and safety improves.
[0055] Moreover, since it foams to this invention under reduced pressure, while being able to make it foam enough with a little foaming agent, a compound with small thermal conductivity with large molecular weight can be used as a foaming agent, and the heat insulation foam which has adiathermic [outstanding] can be efficiently obtained from the ability of the degree of vacuum in a closed cell to be further made high for a short time.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] In conventional heat insulation foam, absorption of the foaming agent by resin having taken place, having connected this with the swelling of the resin section, and having not maintained detailed air bubbles and thin box-frame construction, but having un-arranged [to which a heat insulation property falls], since the inside of the closed cell of polyurethane foam was filled with the foaming agent near ordinary pressure. In order for the part which returns to ordinary temperature or becomes to liquefy and to carry out the adhesion dissolution at resin even if it evaporates with the heat of reaction at the time of polyurethane formation at the time of foaming if a foaming agent with the comparatively high boiling point is used especially, the fall of heat insulation property tends to take place. For example, the vapor pressure in a closed cell [in / in the cyclopentane (49 degrees C of boiling points) used as a hydrocarbon system foaming agent / 25 degrees C] is more than 300mmHg extent, and about the one half of the amount used for foaming has liquefied.
[0004] Moreover, the foaming agent with the pressure of the foaming agent which remains in heat insulation foam high [many] since many are inflammability of a hydrocarbon system will increase the ignition at the time of manufacture and use, and the danger of explosion. Furthermore, if hydrocarbons other than a cyclopentane are used as a foaming agent, what has molecular weight lower than this has thermal conductivity highly difficult [for the top where the boiling point is low] to use. Moreover, some which have high molecular weight had the problem that stopped evaporating with the heat of reaction of polyurethane easily, and the duty of a foaming agent was not achieved according to the boiling point being high, although thermal conductivity was low.
[0005] This invention aims at offering the heat insulation foam which there is no swelling of the resin by the foaming agent liquefied within air bubbles in view of the above, and consists of adiathermic outstanding hard foaming urethane resin. This invention is also set again, when using an inflammable foaming agent, and it aims at offering the heat insulation foam by which the ignition at the time of manufacture and use and the danger of explosion were reduced. This invention aims at offering the approach of it being efficient and manufacturing the heat insulation foam which consists of hard foaming urethane resin which has the adiathermic outstanding closed cell.

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MEANS

[Means for Solving the Problem] The heat insulation foam of this invention consists of hard urethane resin foam which has a closed cell containing a foaming agent, and the pressure of the gasificated foaming agent which is contained in said closed cell is characterized by being 100 or less mmHgs at 25 degrees C.
[0007] Here, said foaming agent is a with a molecular weight of 70 or more compound in 150 degrees C or less of boiling points, and it is desirable for the pressure of the gasificated foaming agent which is contained in a closed cell to be 1 or more mmHgs at 25 degrees C.
[0008] Moreover, as for said foaming agent, it is desirable that it is the compound chosen from the group which consists of a hydrocarbon which has the cyclic hydrocarbon and the 4th class carbon structure of having one or more rings.
[0009] In other modes of the above-mentioned heat insulation foam, said foaming agent is the compound of 170 degrees C or less of boiling points, and the pressure of the gasificated foaming agent which is contained in said closed cell is 1 or less mmHg at 25 degrees C.
[0010] Furthermore, as for said foaming agent, it is desirable that it is the compatibility compound which dissolves in polyol. Such a compatibility compound has the desirable compound chosen from the group which consists of ester, the ether, a tertiary amine, and a ketone.
[0011] The manufacture approach of the heat insulation foam of this invention mixes at least one sort of with a molecular weight of 70 or more liquids at a rate of 0.4 mols/kg or less to polyol by 150 degrees C or less of boiling points as a foaming agent. The mixture furthermore mixed with the poly isocyanate is made to react into the container which can be sealed. It faces forming the rigid urethane foam which said foaming agent is made to evaporate and foam with the heat of reaction of said polyol and said poly isocyanate, and has a closed cell. By controlling the pressure in said container so that the diameter of air bubbles is set to 10 micrometers or more 300 micrometers or less, while decompressing the pressure in said container using a vacuum pump and making it foam by the pressure of 300 or less mmHgs It is characterized by making it filled up with said foaming agent in said closed cell, so that it may become the pressure of 100 or less mmHgs at 25 degrees C.
[0012] In here, said foaming agent is the compound of 95 degrees C or more of boiling points, and it is desirable to make foaming temperature in said container into the temperature of 60 degrees C or more.
[0013] Moreover, as for said foaming agent, it is desirable to use the compound chosen from the group which consists of cyclic ether which has the hydrocarbon which has two or more rings, and two or more oxygen.
[0014] Furthermore, the manufacture approach of the heat insulation foam of this invention mixes at least one sort of liquids of 170 degrees C or less of boiling points as a foaming agent at a rate of 0.004 mols/kg or less to polyol. The mixture furthermore mixed with the poly isocyanate is made to react into [which can be sealed] a container. It faces forming the rigid urethane foam which said foaming agent is made to evaporate and foam with the heat of reaction of said polyol and said poly isocyanate, and has a closed cell. Decompress the pressure in said container using a vacuum pump, and foaming is started by the pressure of 300 or less mmHgs. While considering as the pressure of 0.1 or less mmHgs at the time of foaming termination, the

pressure in said container is controlled so that the diameter of air bubbles is set to 10 micrometers or more 300 micrometers or less, and you make it filled up so that it may become the pressure of 1 or less mmHg at 25 degrees C about said foaming agent in said closed cell.
[0015] Moreover, in the manufacture approach of the heat insulation foam of this invention, a foaming agent is a reactant foaming agent and it is desirable after reaction / foaming process of polyurethane that said reactant foaming agent is solidified by the cellular wall surface, and the inside of air bubbles is decompressed.

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OPERATION

[Function] The heat insulation foam of this invention has the configuration by which the foaming agent gasificated in the closed cell as mentioned above was filled up with 25 degrees C by the pressure of 100 or less mmHgs. Since there are few amounts of the foaming agent which exists as a gas in air bubbles, swelling of the resin part accompanying the dissolution to the resin of a foaming agent cannot happen easily, and detailed air bubbles and thin box-frame construction are maintained. Consequently, the outstanding heat insulation property is realized. Moreover, since there are few amounts of foaming agents which remain in heat insulation foam, even if a foaming agent is inflammability, the flammability of heat insulation foam falls and the safety to the combustion at the time of use improves.
[0017] Moreover, it sets like 1 voice, a foaming agent is a with a molecular weight of 70 or more compound in 150 degrees C or less of boiling points, and the especially desirable pressure of the heat insulation foam of this invention with which said gasificated foaming agent is filled up in a closed cell is 1 or more mmHgs. According to this configuration, the molecular weight of a foaming agent can make it foam enough using the gas more than cyclopentane (molecular weight 70.14) extent. Consequently, thermal conductivity is low and serves as heat insulation foam which has the outstanding heat insulation property. The configuration of such a foaming heat-insulating element is realized by the first manufacture approach of this invention.
[0018] Furthermore, in other especially desirable modes of the heat insulation foam of this invention, a foaming agent is the compound of 170 degrees C or less of boiling points, and the pressure with which the foaming agent gasificated in the closed cell is filled up is 1 or less mmHg. According to this configuration, since the degree of vacuum in a closed cell is high, the heat insulation property which was very excellent is realized. Such a foaming heat-insulating element is realized by the second manufacture approach of this invention.
[0019] Moreover, when it is the compatibility compound which a foaming agent dissolves in polyol, it is desirable in order to give uniform and detailed cellular structure on the occasion of foaming under reduced pressure.
[0020] In the first manufacture approach of this invention, since a with a molecular weight of 70 or more liquid is used as a foaming agent at 150 degrees C or less of boiling points and it foams under reduced pressure of 300 or less mmHgs, under ordinary pressure, foaming which was excellent also in the foaming agent which does not evaporate and foam easily [since the boiling point is high], using this as a foaming agent since the boiling point fell with reduced pressure becomes possible. When using a foaming agent with the higher boiling point at this time, foaming becomes possible by making the pressure in the container at the time of foaming still lower than 300mmHg(s).
[0021] Moreover, under reduced pressure, since it is larger than the case where the volume when evaporating is ordinary pressure, foaming using a little foaming agent also becomes possible. Furthermore, only with the heat of reaction of resinification, since the specific heat, heat of vaporization, etc. are usually large, in order that a foaming agent with difficult foaming may also use only small quantity, it has the big description of a required heating value decreasing and it being said possible that foaming becomes. Moreover, as a foaming agent, the thing of 150 degrees C or less of boiling points when the vapor pressure in 25 degrees C is set to 1 or more

mmHgs is used so that the pressure of a restoration gas may be set to 1 or more mmHgs. Good foaming is attained by carrying out like this. Moreover, since the amount of the foaming agent to be used is 0.4 mols/kg or less to polyol, even when a foaming agent with high vapor pressure with molecular weight comparatively low at about 70 is used, the pressure of the foaming agent in a closed cell is set to 100 or less mmHgs.

[0022] This first manufacture approach adjusts the diameter of air bubbles by controlling whenever [in the container which performs foaming further / reduced pressure] using a vacuum pump. By controlling whenever [reduced pressure], it becomes possible to decide the timing of a polyurethane formation reaction and foaming suitably, and has the very important description that the suitable diameter of air bubbles is realized. As for this, in the case of foaming under ordinary pressure, formation of polyurethane and the timing of foaming are contrastive with having been decided in the boiling point of a foaming agent. That is, since foaming becomes slow and resin becomes hard even if air bubbles become large, heat required for foaming at a polyurethane formation reaction will not be obtained if the boiling point is too high or it is obtained, since resin is too soft, if the boiling point of a foaming agent is low and foaming is too early under ordinary pressure, sufficient increment in the volume does not take place. Therefore, only the foaming agent which has the boiling point from room temperature extent to about 50 degrees C was used. When the diameter of air bubbles is small, it is made early, as compared with the diameter of air bubbles of the foaming agent which the timing of suitable foaming changes the stage and rate of the reduced pressure initiation by the vacuum pump, and is obtained, when large, it is made later, and it is determined experimentally. At this time, although the diameter of air bubbles is adjusted to small 300-micrometer or less value of 10 micrometers or more in order to acquire a good heat insulation property, its about 60 micrometers are desirable from the ease of control.

[0023] Moreover, it is desirable to foam at the high temperature of 60 degrees C or more in this first manufacture approach using the foaming agent of 95 degrees C or more of boiling points as mentioned above. Since it is not necessary to make the pressure in a container extremely low, adjustment of the container internal pressure at the time of foaming becomes easy, and the diameter of air bubbles is made as for it to homogeneity. Moreover, since the boiling point can use effectively the very small gas of thermal conductivity with large molecular weight above 95 degrees C, the heat insulation foam superior to that of a heat insulation property is obtained.

[0024] In the second manufacture approach of this invention, in order to make it foam under reduced pressure, the increment in the volume is large, and foaming sufficient with the foaming agent of the ultralow volume of 0.004 mols/kg is attained to polyol. Moreover, this second manufacture approach adjusts the diameter of air bubbles by controlling whenever [in the container which performs foaming / reduced pressure] like the first manufacture approach using a vacuum pump. Therefore, it has the very important description that decide the timing of a polyurethane formation reaction and foaming suitably by controlling whenever [reduced pressure] similarly, and control of the diameter of air bubbles is attained. However, since there are very few amounts of the foaming agent to be used, after foaming initiation must fully lower a pressure by the time of foaming termination, and the pressure at the time of foaming termination is set to 0.1 or less mmHgs.

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EXAMPLE

[Example] Next, this invention is explained based on a desirable example. In this invention, especially the thing for which the thermal conductivity of a foaming agent is reduced, it is 150 degrees C or less of boiling points and 70 or more molecular weight as a foaming agent, and a compound with larger molecular weight than cyclopentane extent is used in order to raise the heat insulation property of the foam obtained, and the pressure of the gasificated foaming agent in a closed cell is set to 1 or more mmHgs is desirable. When this has the too low pressure of a with a molecular weight [in a closed cell] of 70 or more gas, it is because it becomes impossible to disregard existence of the residual gas as an impurity with high thermal conductivity with small molecular weight within a closed cell.
[0026] The hydrocarbon which has the cyclic hydrocarbon or the 4th class carbon structure of having one or more rings from a viewpoint of thermal conductivity, as a with a molecular weight of 70 or more compound at 150 degrees C or less of boiling points is desirable for improvement in a heat insulation property. As this example, there are the cyclopentane (molecular weight 70.14, 49 degrees C of boiling points) of a cyclic hydrocarbon, a cyclohexane (molecular weight 84.16, 80.7 degrees C of boiling points), a cyclohexene (molecular weight 82.15, 83 degrees C of boiling points), 1, 4-cyclohexadiene (molecular weight 80.13, 81 degrees C of boiling points), 1, 3-cyclohexadiene (molecular weight 80.13, 80 degrees C of boiling points), bicyclo heptadiene (molecular weight 92.14, 89 degrees C of boiling points), NORUBONIREN (molecular weight 94.16, 96 degrees C of boiling points), Moreover, as a hydrocarbon which has the 4th class carbon structure, there is a 2 and 2-dimethyl butane (molecular-weight 86.18, 50 degrees C of boiling points), 2, and 3-dimethyl-2-butene (molecular weight 84.16, 73 degrees C of boiling points) etc.
[0027] Furthermore, especially since [that molecular weight is large] the fluorinated compound has low thermal conductivity, it is desirable. As this example, there are a perfluoro decalin (molecular weight 462.1, 141 degrees C of boiling points), a perfluoro methylcyclohexane (molecular weight 350.7, 78 degrees C of boiling points), perfluoro methylcyclopentane (molecular weight 300.05, 57 degrees C of boiling points), etc.
[0028] Moreover, in the heat insulation foam of this invention, the gasificated foaming agent is smaller than molecular weight 70, and especially the configuration whose pressure with which this gasificated foaming agent is filled up in a closed cell is 1 or less mmHg is desirable. Usually, although the foaming agent with molecular weight smaller than 70 is unsuitable as a foaming agent for heat insulation foam since molecular weight is small, and thermal conductivity is high, it is making filling pressure in a closed cell extremely low, and serves as heat insulation foam which has the outstanding heat insulation property.
[0029] Moreover, in order to form a closed cell uniform and detailed as a foaming agent of the heat insulation foam of this invention described so far, the compound which has polyol and compatibility is desirable. As this compatibility compound, there are ester, the ether, a tertiary amine, and a ketone. For example, there are methyl propionate (molecular weight 88.11, 79 degrees C of boiling points), methyl iso butyrate (molecular weight 102.13, 90 degrees C of boiling points), a tetrahydrofuran (molecular weight 72.11, 66 degrees C of boiling points), 1, 3-dioxolane (molecular weight 74.08, 74 degrees C of boiling points), triethylamine (molecular weight 101.19, 89 degrees C of boiling points), 3-methyl-2-butanone (molecular weight 86.13, 93

degrees C of boiling points), etc.
[0030] There are two kinds of following manufacture approaches as an approach of realizing the configuration of especially desirable heat insulation foam described above. The first manufacture approach mixes further with the poly isocyanate what mixed the with a molecular weight of 70 or more liquid at a rate of 0.4 mols/kg or less to polyol by 150 degrees C or less of boiling points as a foaming agent, and carries out evaporation foaming of this within the container which was decompressed using the vacuum pump and which can be sealed. In order to foam under reduced pressure, it foams to the efficient big volume and becomes that what is necessary is just to use a foaming agent 0.4 mols [/kg] or less to polyol as a result. Moreover, at the time of this evaporation foaming, the pressure in a container is too high, and foaming is overdue, or the diameter of air bubbles is controlled by adjusting to a moderate pressure so that it is too low and growing gigantic of bumping or air bubbles does not take place. To polyol, since it is few in kg and 0.4 mols /or less, the maximum vapor tension in air bubbles also falls, and the amount of the foaming agent to be used becomes the pressure of 100 or less mmHgs. Since what has large molecular weight has the boiling point and large heat of vaporization, it does not fully foam only with the heat obtained at the reaction of the poly isocyanate and polyol in many cases, but in order to end with the heat which provides the temperature up of a little foaming agent, and evaporation according to this approach, foaming takes place easily.
[0031] Moreover, if the pressure in air bubbles becomes small too much as already stated, the effect of a gas with small thermal conductivity, such as air which is an impurity, may come out, and a heat insulation property may worsen. Therefore, the pressure in air bubbles needs to have 1 or more desirable mmHgs, the boiling point of a foaming agent needs to be 150 degrees C or less in this case, and the amount used needs to be 0.004 mols/kg or more to polyol. In the same reason, as for the pressure in air bubbles, it needs to be still more desirable that they are 10 or more mmHgs, the boiling point of a foaming agent needs to be 115 degrees C or less in this case, and the amount of foaming agents needs to be 0.04 mols/kg or more. Moreover, since it becomes easy for the one to some extent where the boiling point is higher to control foaming, without being influenced by the temperature decided with heat of reaction in order to make it foam under reduced pressure like this invention and to control a foaming stage, 75 degrees C or more of boiling points are desirable.
[0032] Moreover, about the first manufacture approach of this heat insulation foam, it is desirable to make it foam at the temperature of 60 degrees C or more using at least one kind of liquid of 95 degrees C or more of boiling points as a foaming agent. The molecular weight of the liquid of 95 degrees C or more of boiling points is also large, since the thermal conductivity of a gaseous state is also small, it is desirable as a foaming agent, but since maximum vapor tension is low, it needs to keep still lower the pressure in the container at the time of foaming compared with the low thing of the boiling point. However, if the heat insulation foam raw material containing a foaming agent is poured in, with change of that vapor pressure and volume in a container, the pressure in a container will be changed, and the rate of this pressure fluctuation is so large that an early pressure is low, and this will produce the heterogeneity of the air bubbles in heat insulation foam, and will tend to lead to the fall of a heat insulation property. Therefore, an initial pressure is maintained at a to some extent high pressure, and manufacture of heat insulation foam becomes [the direction which raises the temperature at the time of foaming] easy. It is 60 degrees C or more in temperature, and is the container internal pressure 100 - more than 200mmHg extent, and by making it foam, the diameter of air bubbles is uniform and, specifically, heat insulation foam excellent in heat insulation property is obtained easily. Moreover, if the high thing of OH ** is used as polyol, temperature of the reaction time of the poly isocyanate and polyol can be made high, and, thereby, can set up foaming temperature highly.
[0033] It is possible to use suitably the cyclic ether which has the hydrocarbon which has two or more rings, or two or more oxygen as a liquid of 95 degrees C or more of boiling points. such a hydrocarbon and cyclic ether — carrying out — there is KUADORISAI clan (molecular-weight 92.14, 108 degrees C of boiling points), 1,4-dioxane (molecular-weight 88.1, 101 degrees C of boiling points), 1, and 4-JIOKISEN (molecular weight 86.1, 95 degrees C of boiling points) etc.

[0034] Moreover, it is desirable for the pressure with which the foaming agent gasificated in the closed cell is filled up as heat insulation foam of this invention especially to be 1 or less mmHg. The heat insulation property which was excellent since the degree of vacuum in a closed cell was very high as already stated is realized. The configuration of such a foaming heat-insulating element is realized by the second manufacture approach of this invention. In this approach, although it is made to foam under reduced pressure as well as the first manufacture approach, there is the description which makes the foaming agent of the ultralow volume of 0.004 mols/kg foam to a product generally by the quite low pressure to polyol. Thus, since the foaming agent to be used is a minute amount, the pressure of the foaming agent which remains in a closed cell becomes very low with 1 or less mmHg. Moreover, there is the very important description that control becomes possible about the diameter of air bubbles by adjusting a pressure and taking the timing of an urethane formation reaction and foaming also by this second manufacture approach. Moreover, since there are few amounts of a foaming agent, there can be little energy which evaporation takes, and can end and the boiling point can also use the high, large compound of heat of vaporization. Moreover, since foaming will become difficult if too few, as for the amount of a foaming agent, it is desirable to use 0.001 mols /or more kg.
[0035] In addition to the foaming agent used by the first manufacture approach, the foaming agent which has the boiling point in a 150 to 170 degrees C pyrosphere can be used for the foaming agent used for the second manufacture approach of this this invention. This is because the vapor pressure in a closed cell becomes low and there should just be vapor pressure in 25 degrees C more than 0.2mmHg extent. Moreover, a foaming agent with high thermal conductivity with small molecular weight can also be used. This has a pressure as low as 1 or less mmHg in air bubbles, and is because it becomes regardless of the heat insulation property of heat insulation foam at the thermal conductivity of the gas in a closed cell. As a concrete foaming agent, there are a dicyclopentadiene (molecular weight 132.21, 170 degrees C of boiling points), a perfluoro-1-methyl decalin (molecular weight 512.11, 159 degrees C of boiling points) to have the boiling point in a pyrosphere, etc. Moreover, about what has low molecular weight, since control of foaming under reduced pressure will become difficult if the boiling point is too low, it is desirable to have the boiling point about 50 degrees C or more. Moreover, since there are very few amounts of the foaming agent used by this second manufacture approach, mixing with polyol more at homogeneity is important for a foaming agent, and its compatibility compounds, such as the ether excellent in compatibility with the already described polyol, a ketone, and tertiary amine, are desirable especially as a foaming agent.
[0036] Moreover, in order to prevent the heat insulation property of a foaming heat-insulating element worsening when gases, such as air with high thermal conductivity other than a foaming agent, blend, it is desirable to permute the inside of the container made reduced pressure with the foaming agent gasificated beforehand. Moreover, a foaming agent may consist of a reactant foaming agent in the heat insulation foam of this invention. A reactant foaming agent is a foaming agent solidified by a certain chemical reaction after foaming, it mixes with an urethane raw material and this is used. In this way, the heat insulation foam which the inside of air bubbles was decompressed and excelled [solidify / this reactant foaming agent / by the cellular front face] in the heat insulation property is obtained after the foaming process of polyurethane. As such a reactant foaming agent, the compound which has either [at least] an amino group or a hydroxyl group is desirable, and these compounds delay a stage from foaming and are solidified by reacting with the poly isocyanate. It is also possible to make it foam using the liquid of polymerization nature as a foaming agent, to delay a stage otherwise, and to carry out polymerization immobilization of the foaming agent according to an operation of a polymerization catalyst.
[0037] As an approach of making a stage delaying and solidifying from foaming, the compound which has an amino group or a hydroxyl group is used as a core, and after destroying a microcapsule with the heat of reaction of the poly isocyanate and polyol as a wallplate and a microcapsule and making thermoplastics foam, the approach of solidifying by the reaction with the poly isocyanate is. It is effective for others to use tertiary alcohol with a comparatively slow reaction with the poly isocyanate etc. After making tertiary alcohol etc. foam with the heat of

reaction of the poly isocyanate and polyol, it is possible to make said alcohol and isocyanate react and to solidify. Moreover, a phenol, a thiol, a carboxylic acid, an acid amide, etc. are one of those have slow a reaction although it reacts with isocyanate and possible using as a reactant foaming agent. As alcohol suitably used especially as a reactant foaming agent, there are a tertiary butanol (molecular weight 74.12, 83 degrees C of boiling points), hexafluoro-2-methyl isopropanol (molecular weight 182.0, 60 degrees C of boiling points), and a perfluoro tertiary butanol (molecular weight 236.05, 44 degrees C of boiling points).
[0038] Moreover, in the case of the heat insulation foam for refrigerators, the container used with the configuration of this invention described in the top usually consists of a metallic cabinet and an inner case made of resin. Although the pressure of several 100 mmHg(s) joins this container at the time of reduced pressure, it is possible to prevent the big deformation by said pressure impression by choosing the structure containing the ingredient and thickness of a tank and an inner case. Or not only the inside of a container but the outside of a container and the approach except the pressure which joins a container as reduced pressure can also be used. Moreover, after resin spreads in a large area for evasion of bumping, or uniform cellular formation, it can also be made to foam at the time of impregnation of the resin raw material containing polyol and the poly isocyanate. Furthermore, after pouring in a resin ingredient, it becomes possible by carrying out reduced pressure control of the inside of a container gradually.

[0039] In order that the polyol used for this invention may obtain a degree of hardness besides the polyether system polyol currently used conventionally and polyester system polyol, or in order to control reactivity, the polyol which has in intramolecular many hydroxyl groups compounded from polyhydric alcohol is suitable. Moreover, since there are few amounts of the foaming agent to be used, polyol with low viscosity is desirable. The poly isocyanate to which a diphenylmethane diisocyanate system, a tolylene diisocyanate system, a xylylene diisocyanate system, a meta-xylylene diisocyanate system, a hexamethylene di-isocyanate system, the lysine diisocyanate system, the isophorone diisocyanate system, the trimethyl-hexamethylene-di-isocyanate system, the dimer acid diisocyanate system, etc. are suitable, and the isocyanate used for this invention gave these fire retardancy is most suitable.
[0040] The catalyst used in this invention is good to choose the most effective catalyst with the reactivity of an urethane raw material, such as a gelation catalyst, a bubble-ized catalyst, and a delay catalyst. Although the catalysts generally used are the third class amine and an organometallic compound, there are amines monoamines, diamines, triamine, annular amines, and alcoholic, ether amines, etc. in an amine system catalyst. In an organometallic compound, an organic tin compound is used best. The catalyst for a general formula is used in this invention. However, it is required to mix the catalyst of various kinds [**** / using properly depending on the boiling point]. Moreover, the foam stabilizer used for this invention has a common alkyl SHIRAN polyoxyalkylene copolymer. A silicon system foam stabilizer shows the outstanding addition effectiveness, although the effectiveness differs. In addition, the compatibility of a raw material is raised and it becomes a cellular nucleus, and if surface tension is reduced and the air bubbles under foaming are stabilized, it can use.
[0041] the following concrete examples — setting — as Catalyst A — the Kao Corp. make — as KAORAIZA No.1 and a foam stabilizer A — the poly isocyanate of amine equivalent 170 was used as hydroxyl value 600 mgKOH/g and poly isocyanate A by aromatic amine system polyether polyol as hydroxyl value 500 mgKOH/g and polyol B by aromatic amine system polyether polyol as the product F373 made from Shin-etsu Chemistry, and polyol A.
[0042] In [example 1] this example, the heat insulation foam to which it comes to fill up this foaming agent by the pressure of 100 or less mmHgs in a closed cell at 150 degrees C or less of boiling points using a with a molecular weight of 70 or more foaming agent was formed under reduced pressure. The weight ratio of the used raw material is as follows. Polyol A / foam stabilizer A / catalyst A / foaming agent A / poly isocyanate =100/3/2/2.8/165. 2 and 2-dimethyl butane (molecular weight 86.2, 50 degrees C of boiling points) which is the hydrocarbon which has the 4th class carbon structure as a foaming agent A was used. The concentration to the polyol of a foaming agent is 0.4 mols/kg. First, Polyol A, Catalyst A, and the foam stabilizer A

were mixed, and the poly isocyanate A was mixed further. This resin raw material was poured in from that inlet into the container which consists of a metallic cabinet and an inner case made of resin and which can be sealed, and foaming of the hard urethane heat insulation foam was carried out. At this time, the inside of a container was beforehand changed into the reduced pressure condition of 400mmHg(s) through the exhaust port with the vacuum pump. After impregnation, the inlet exhausted according to advance of a polyurethane formation reaction, and performed foaming by the pressure of 300 or less mmHgs so that it might close and fluctuation of the pressure in a container might become small by the valve installed in the exhaust port. In addition, the pressures in the container at the time of foaming initiation were 300mmHg(s), and temperature was 30 degrees C. After foaming finished, it was left on the 1st, making the inside of a container reduced pressure. In this way, the pressures in the air bubbles which ground the obtained heat insulation foam and were computed from the amount of foaming agents which came out, and the volume of the air bubbles for which it asked from the consistency of foam and resin were 90mmHg(s). Moreover, the diameter of average air bubbles of a closed cell was 220 micrometers.

[0043] By the formula of polyol / foam stabilizer A / catalyst A / foaming agent A / poly isocyanate =100/3/2/22/165, the weight ratio of the [example 1 of comparison] raw material performs foaming to the bottom of ordinary pressure. The concentration to the polyol of a foaming agent is 0.4 mols/kg. In this way, when cellular internal pressure was computed like the example 1 about the obtained foam, it had liquefied about the one half of the foaming agent used by 320mmHg.

[0044] Heat insulation property was compared as follows before grinding about the foam obtained in the example 1 and the example 1 of a comparison. That is, in the 25-degree C interior of a room, heat insulation foam with a thickness of 5cm was carried on the 50-degree C hot plate, and the temperature gradient of the top face and inferior surface of tongue was measured. From the comparison of the thermal conductivity for which it asked from this temperature gradient, the heat insulation foam of an example 1 was excellent in the heat insulation property 8% compared with the heat insulation foam of the example 1 of a comparison. Moreover, when the fire-resistant sex test was performed, the heat insulation foam of an example 1 showed fire retardancy better than the heat insulation foam by which foaming was carried out under the ordinary pressure of the example 1 of a comparison. Since suitable cellular structure was formed by that there are few amounts of the foaming agent contained in the closed cell of foam, and there are also few amounts of the foaming agent to liquefy since the heat insulation foam of an example 1 is foaming using a little foaming agent under reduced pressure, and having performed timing of a polyurethane formation reaction and foaming by accommodation of whenever [reduced pressure], this is considered.

[0045] In [example 2] this example, the compound which has polyol and compatibility as a foaming agent is used. The weight ratio of the used raw material is as follows. Polyol A / foam stabilizer A / catalyst A / foaming agent B / poly isocyanate =100/3/2/2.8/165. As a foaming agent B, the ether system compound tetrahydrofuran with polyol and compatibility was used. The concentration to the polyol of a foaming agent is 0.39 mols/kg. Heat insulation foam was obtained almost like the example 1. However, foaming was performed under the pressure of 200 or less mmHgs. The pressures at the time of foaming initiation were 200mmHg(s), and temperature was 50 degrees C. When the pressure in the air bubbles of the obtained foam was computed like the example 1, it was 80mmHg(s). Moreover, the diameter of average air bubbles of a closed cell was 110 micrometers. About the obtained heat insulation foam, fire retardancy and a heat insulation property were measured like the example 1. About fire retardancy, good fire retardancy was shown compared with the example 1 of a comparison like the example 1. Moreover, about the heat insulation property, it improved 20% as compared with the example 1. Compatibility with polyol becomes good by using an ether system compound as a foaming agent, and since uniform and detailed air bubbles were formed, the improvement in this heat insulation property is considered.

[0046] In [example 3] this example, the reactant foaming agent which has a hydroxyl group as a foaming agent is used. The weight ratio of the used raw material is as follows. Polyol A / foam

stabilizer A / catalyst A / foaming agent C / poly isocyanate =100/3/2/2.7/180. The tertiarybutyl alcohol which has a hydroxyl group was used as a foaming agent C. The concentration to the polyol of a foaming agent is 0.36 mols/kg. Moreover, it permuted so that 200mmHg hidden total pressure might be beforehand set to 240mmHg(s) in the steam of the foaming agent tertiarybutyl alcohol which uses the inside of a container. Moreover, the pressure at the time of foaming initiation was made to 150mmHg(s), temperature was made into 45 degrees C, and it was made to foam by the pressure of 150 or less mmHgs. Others formed heat insulation foam like the example 1. When the pressure in the air bubbles of the obtained foaming heat-insulating element was computed like the example 1, it was 1 or less mmHg. Moreover, the diameter of average air bubbles of a closed cell was 80 micrometers.

[0047] Heat insulation foam was formed using the tertiarybutyl alcohol as a foaming agent C under the [example 2 of comparison] ordinary pressure. In addition, the container preceded paying a polyurethane raw material and was heated at 50 degrees C. The weight ratio of the used raw material is as follows. Polyol A / foam stabilizer A / catalyst A / foaming agent C / poly isocyanate =100/3/2/30/180.

[0048] Fire retardancy and a heat insulation property were measured about the heat insulation foam obtained in the example 3 and the example 2 of a comparison. The heat insulation foam of an example 3 showed good fire retardancy compared with the example 2 of a comparison. Moreover, about the heat insulation property, it improved 32% compared with the example 2 of a comparison. Moreover, the example 2 of a comparison of the time amount needed after foaming by the time it reached the aforementioned heat insulation property, i.e., the time amount which a reactant foaming agent requires for solidifying enough, was as longer as 5 times of the foaming heat-insulating element of an example 3. The solid state of the tertiarybutyl alcohol which is the reactant foaming agent which has the hydroxyl group used as a foaming agent progresses more efficiently, and since the pressure in air bubbles reached the high degree of vacuum by having fallen further, the improvement in this heat insulation property is considered. Since it foamed under reduced pressure, this has the little amount of the foaming agent which should be solidified, ends, and is considered because the solid state progressed efficiently as a result.

[0049] In [example 4] this example, using the compound of 95 degrees C or more of boiling points as a foaming agent, temperature at the time of foaming was made into 60 degrees C or more, and heat insulation foam was formed. The weight ratio of the used raw material is as follows. Polyol B / foam stabilizer A / catalyst A / foaming agent D / poly isocyanate =100/3/2/3.4/165. As a foaming agent D, the boiling point used the hydrocarbon KUADORISAI clan (molecular weight 92.14, 108 degrees C of boiling points) 95 degrees C or more. The concentration to the polyol of a foaming agent is 0.37 mols/kg. The pressure in 69 degrees C and a well-closed container was set to 100mmHg(s) for the temperature at the time of foaming initiation, and also heat insulation foam was obtained like the example 1. When the pressure in the air bubbles of the obtained foaming heat-insulating element was computed like the example 1, it was 33mmHg(s). Moreover, the diameter of average air bubbles of a closed cell was 35 micrometers.

[0050] Foaming was tried by the formula of the following [the bottom of the [example 3 of comparison] ordinary pressure]. Polyol B / foam stabilizer A / catalyst A / foaming agent D / poly isocyanate =100/3/2/30/180. However, foaming did not fully take place but the volume of heat insulation foam became small.

[0051] Fire retardancy and a heat insulation property were measured about the heat insulation foam obtained in the example 4 and the example 3 of a comparison. About fire retardancy, the direction of an example 4 showed good fire retardancy compared with the example 3 of a comparison. Moreover, the heat insulation property of an example 4 improved 90% 20% compared with the example 3 of a comparison as compared with the example 1. It is made 60 degrees C or more by the thermal conductivity of the gas in a closed cell having fallen upwards, since the compound which has the boiling point 95 degrees C or more as a foaming agent was used, and it is whenever [comparatively high reduced pressure], and since high quality heat insulation foam was obtained, it is considered [since foaming advanced, control of container internal pressure becomes easy, the improvement in this heat insulation property is uniform and].

[0052] In [example 5] this example, the high heat insulation foam of the degree of vacuum in a closed cell was formed using the foaming agent of ultralow volume. The weight ratio of the used raw material is as follows. Polyol A / foam stabilizer A / catalyst A / foaming agent E / poly isocyanate =100/3/2/0.02/180. The acetone (molecular weight 58.0) was used as a foaming agent E. The concentration to the polyol of a foaming agent is 0.0034 mols/kg. Before pouring the above-mentioned resin raw material into a container, the inside of a container was decompressed through the exhaust port with the vacuum pump, the acetone was poured in so that the acetone steam of 270mmHg might exist, total pressure in an early container was set to 330mmHg(s), and also foaming was performed like the example 1. In addition, the pressures at the time of foaming initiation were 220mmHg(s), and temperature was 40 degrees C. Moreover, the pressure in the exhaust port at the time of the completion of foaming was 0.1 or less mmHgs.

[0053] In this way, when the pressure in the air bubbles of the obtained heat insulation foam was computed like the example 1, it was 1 or less mmHg. Moreover, the diameter of average air bubbles of a closed cell was 70 micrometers. Moreover, fire retardancy and a heat insulation property were measured about the obtained heat insulation foam. The heat insulation foam of an example 5 showed good fire retardancy like the example 3, and showed [fire retardancy] the good property about the heat insulation property as well as an example 3. Since the amount of a foaming agent is a minute amount and ended by foaming under reduced pressure, this good fire retardancy and a heat insulation property are considered because the degree of vacuum in the closed cell of the obtained heat insulation foam became high.

[Translation done.]